

Copper(I) Cluster of Aggregation-induced Emission and X-Ray Scintillator Characteristic

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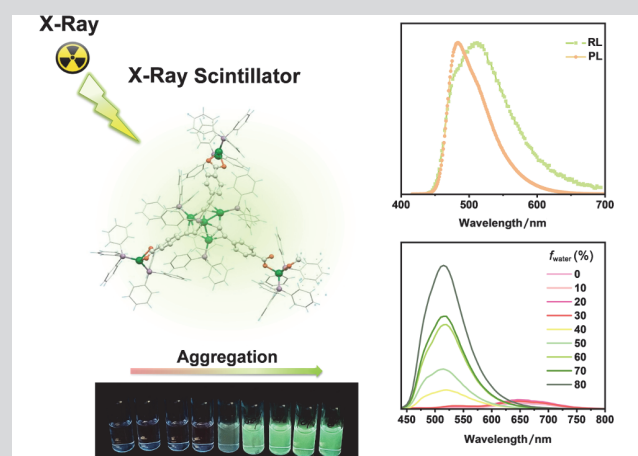
Received May 30, 2024

Accepted June 25, 2024

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Due to their precise atomic structures, photoluminescent copper nanoclusters (Cu NCs) have promising applications in basic research and technical applications, such as bioimaging, cell labeling, phototherapy, and photoactivation catalysis. In this work, we report a simple strategy for synthesizing novel CuNCs co-protected by alkynyl and phosphine ligands with the molecular formula $[\text{Cu}_7(\text{PPh}_3)_{10}(\text{PE})_3(\text{CH}_3\text{O})]$ ($\text{Cu}_4@\text{Cu}_3$). Single-crystal X-ray crystallography reveals that the NC core exhibits an open square structure and an overall pyramid shape. Two $\text{Cu}_4@\text{Cu}_3$ units are connected through weak interactions to form dimers in crystals, creating a molecular cage that looks like two tightly closed bowls. $\text{Cu}_4@\text{Cu}_3$ exhibits dual emission in the visible region. It is also an aggregation-induced emission (AIE)-active luminescent substance, which exhibits strong emission in the visible light region when aggregated. Besides, it has the properties of radioluminescent (RL) and could be a potential scintillator material. This study not only enriches the types of atomically accurate AIE clusters, but also holds significant importance for the development of a new

generation of high-performance and environmentally friendly X-ray scintillators.



Keywords Copper nanocluster; Aggregation-induced emission; X-Ray scintillator

1 Introduction

Atomically precise metal (Au, Ag, Cu) nanoclusters exhibit impressive luminescent properties due to their well-defined compositions and structures, including a variety of emission wavelengths, large Stokes shift, high luminescence quantum yield and long emission lifetime, showcasing a wide range of applications in optical devices, biological imaging, sensors, etc.^[1–3] Among these, copper nanoclusters (Cu NCs) have garnered significant attention due to their economic advantages compared to precious metals. Notably, their versatile reactivity with a wide array of ligands and the favorable low-energy ligand-to-metal charge transfer (LMCT) or cluster-centered electronic transitions exhibit remarkable potential. These unique properties have facilitated the development and advancement, such as advancements in

luminescent sensors,^[4–8] catalysis,^[9–13] and self-assembly materials,^[14–16] thereby contributing significantly to the field of optoelectronics and material science. Unfortunately, the development of copper nanoclusters has lagged far behind the well-studied Au and Ag nanoclusters. Due to their sensitivity to air oxidation, preparing stable CuNCs is more challenging compared to Ag and AuNCs.^[17]

The phenomenon of aggregation-induced emission (AIE) in NCs has received much attention.^[18,19] Distinct from the prevalent trend observed in fluorophores, wherein increasing concentration leads to a decline in emission, so-called “aggregation-induced quenching”, some metal NCs exhibit the opposite trend, namely AIE.^[19,20] This phenomenon can be orchestrated through the precise manipulation of solvent polarity, pH, and the incorporation of specific ions, all of which facilitate the self-assembly and aggregation of metal NCs, thereby triggering AIE.^[21–23] Recently, Tang *et al.*^[24] proposed a new concept called “cluster-induced emission”. Therefore, AIE materials have emerged as a novel class of functional materials, exhibiting applicability in diverse fields encompassing biological imaging, organic light-emitting diode (OLED) technology, and chemical sensing, etc.^[25] Xie *et al.*^[26] initially identified

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this phenomenon in Au/Ag NCs, providing foundational insights. Subsequently, Zang *et al* [27] observed AIE in alkynyl protected Cu NCs. In recent years, some researches have reported AIE Cu NCs.[28] However, due to the lack of straightforward methods to obtain strongly photoluminescent and stable Cu NCs, AIE-emitting Cu NCs protected by alkyne are rarely reported.

Here we introduce a facile method for synthesizing air-stable and photoluminescent Cu NCs. The as-synthesized nanocluster, formulated as $[\text{Cu}_7(\text{PPh}_3)_{10}(\text{PE})_3(\text{CH}_3\text{O})]$ (PPh_3 =triphenylphosphine, PE =4-ethynylbenzoic acid) and referred to as $\text{Cu}_4@\text{Cu}_3$, is co-protected by alkynyl and phosphine ligands with a yield of approximately 65% (based on Cu atoms). Single-crystal X-ray diffraction (SC-XRD) analysis of $\text{Cu}_4@\text{Cu}_3$ indicates that the compound forms a dimer with structural features not previously observed in any coinage metal NCs. The cluster exhibits dual emission in the visible region and AIE behavior, meaning it exhibits much stronger emission in the aggregated state than in dilute solution. Besides, it has the properties of radioluminescent (RL) and could be a potential X-ray scintillator material.

2 Experimental

2.1 Materials and Reagents

Triphenylphosphine (PPh_3 , 98%) and tetrakis (acetonitrile) copper(I) hexafluorophosphate ($[\text{Cu}(\text{MeCN})_4(\text{PF}_6)]$, 98%) were purchased from Anhui Zesheng Technology Co., Ltd. (Anqing, China). Triethylamine (Et_3N , 98%) was purchased from Shanghai Merrier Biochemical Technology Co., Ltd. (Shanghai, China). 4-Ethynylbenzoic acid (98%) was purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd. (Shanghai, China). Methanol (CH_3OH , AR.) was employed from Beijing Tongguang Fine Chemical Co., Ltd. (Beijing, China). All reagents and solvents were used as received without further purification.

2.2 Instrumentation

^1H NMR spectra were measured on a Bruker Ascend 400M (400 MHz) Fourier transform NMR spectrometer with chemical shifts (δ , ppm) relative to tetramethylsilane (Me_4Si). UV-Vis spectra were obtained using a UV1050 UV/VIS spectrophotometer. Dynamic light scattering (DLS) experiments were performed using a Zetasizer Nano dynamic light scattering particle size/zeta potential analyzer at room temperature.

Steady-state emission spectra were recorded on an Edinburgh Instrument FLS1000 spectrofluorometer (Edinburgh Instruments Ltd., Edinburgh). Liquid-state

emission and excitation spectra at room temperature were recorded with liquid samples loaded in a quartz tube. The emission lifetime was measured using a microsecond flash-lamp (100 W, Virtual gate), and an EPL picosecond pulsed diode laser (380 nm). All fluorescence spectrogram tests were performed in Ex corrected and Em uncorrected mode. The lifetime (τ) of the luminescence was obtained by fitting the decay curve with a multi-exponential decay function of

$$I(t) = \sum_i A_i e^{-t/\tau_i} \quad (1)$$

where A_i and τ_i represent the amplitudes and lifetime of the individual components for multi-exponential decay profiles, respectively.

X-Ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000 Versa Probe III instrument. Single crystal X-ray diffraction (SCXRD) data of $\text{Cu}_4@\text{Cu}_3$ were collected on a Rigaku XtaLab Pro diffractometer equipped with a Mo $K\alpha$ ($\lambda=0.071073$ nm) radiation source. High-resolution electrospray ionization-time of flight (ESI-TOF) mass spectra were recorded on an AB Sciex Triple ToF 6600 plus mass spectrometer in positive reflection mode. The RL spectra were recorded using a spectrometer (OmniFluo990) equipped with an X-ray tube (tungsten target, Moxtek). The detection slit was set at 3 nm and the X-ray exit was set at 1 cm from the sample for all spectral measurements. All tests were performed in a radiation-tight environment with lead plate shielding.

2.3 Synthesis of $\text{Cu}_4@\text{Cu}_3$

$[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$ (26.25 mg, 0.07 mmol), PPh_3 (26.26 mg, 0.10 mmol), and 4-ethynylbenzoic acid (4.4 mg, 0.03 mmol) were mixed in 4 mL of MeOH. After complete dissolution, Et_3N (40 μL , 0.29 mmol) was added, resulting in the immediate formation of a large quantity of yellow precipitate. After vigorous stirring for 5 min, the resultant solution was filtered. Then, distilled water was added drop by drop to the filtrate until the solution became cloudy. The solution was filtered again, and the filtrate was allowed to slowly evaporate in the dark at room temperature to obtain colorless block crystals. Yield: 65% (23.4 mg), based on $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$. ^1H NMR (400 MHz, DMSO), δ : 7.66–7.59 (m, 6H), 7.59–7.52 (m, 6H), 7.43 (t, $J=7.2$ Hz, 30H), 7.36 (t, $J=7.2$ Hz, 60H), 7.27 (s, 60H). ESI-MS (MeOH), m/z : 1650.1747, (cal.1650.1605) for $[\text{Cu}[\text{M}(\text{PPh}_3)_3(\text{CH}_3\text{O})]]^{2+}$.

3 Results and Discussion

3.1 Synthesis and Characterization

In order to synthesize copper clusters efficiently, we have adopted a one-pot synthesis strategy by reacting $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)]$ with PE, PPh_3 , and Et_3N in the methanol

solution to obtain heptacore copper clusters. After evaporation, colorless block crystals were obtained (Fig. 1A), which were determined to be $\text{Cu}_4@\text{Cu}_3$ by single-crystal X-ray crystallography. The guest species were further identified by NMR characterization (Fig. S1 in the Electronic Supplementary Information, ESI). Its identity was further confirmed by high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) in positive mode. The m/z values observed at 1650.1747 (calcd. 1650.1605) in the ESI mass spectra are assignable to the cluster divalent ions of $\{\text{Cu}[\text{Cu}_7(\text{PPh}_3)_9(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-}p\text{-PhCOO})_3]\}^{2+}$ (Fig. 1B). The experimental isotopic pattern exhibited close agreement with the simulated pattern. The elemental composition of $\text{Cu}_4@\text{Cu}_3$ was further characterized by XPS analysis, revealing the presence of Cu, P, C, and O elements (Fig. S2 in the ESI). The valences of the Cu(I) ions were confirmed by XPS results; the peaks at around 953.34 and 933.52 eV were attributed to Cu(I) (Fig. 1C). Besides, we performed a thermal stability analysis of the compound, and Fig. S3 in the ESI shows that the structure begins to lose weight at 250 °C, and the structure starts to decompose.

Their atomically precise structures were further established by single-crystal X-ray diffraction (SCXRD) analysis (Table S1 in the ESI). $\text{Cu}_4@\text{Cu}_3$ crystallizes in the triclinic $P\bar{1}$ space group and is composed of seven Cu atoms, seven PPh_3 , three PE, and one methanol (Fig. 2F). The four Cu(I) and three PE in the center form a triangular pyramid with an open square structure (Fig. 2A), with Cu1 and three acetylene groups bridged in a μ_3 bridge (Fig. 2B). The distances of Cu1—Cu2, Cu2—Cu3, and Cu2—Cu4 at 2.453, 2.451, and 2.467 Å (1 Å=0.1 nm) are shorter than the distances of

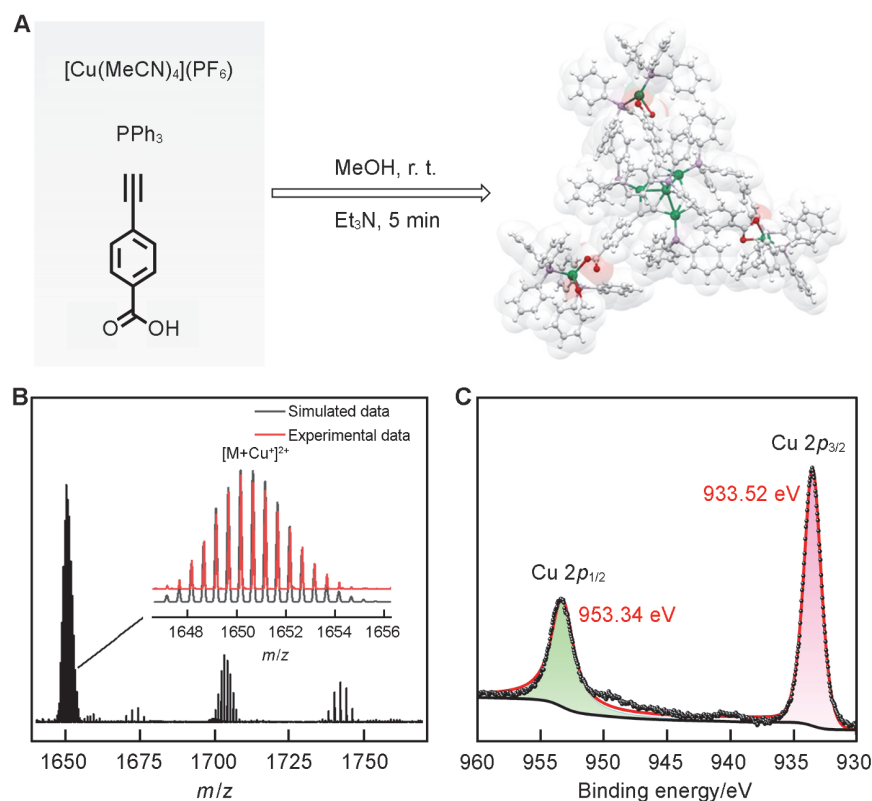


Fig. 1 General synthetic route for $\text{Cu}_4@\text{Cu}_3$ nanocluster (A), positive mode ESI-MS spectrum of $\text{Cu}_4@\text{Cu}_3$ in MeOH (B), and the expanded XPS spectra in the Cu 2p region of $\text{Cu}_4@\text{Cu}_3$ (C)

Inset of (B): enlarged portion of the spectrum showing the measured (red) and simulated (black) isotopic distribution patterns of $\{\text{Cu}[\text{Cu}_4(\text{PPh}_3)_9(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-}p\text{-PhCOO})_3]\}^{2+}$.

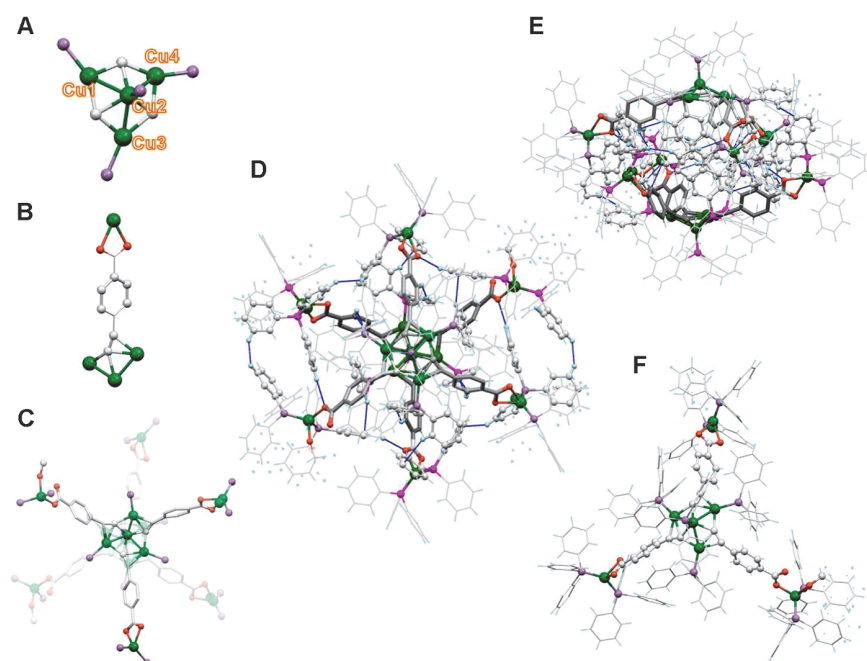


Fig. 2 $\text{Cu}_4@\text{Cu}_3$ centered with an open square structure (A), bonding modes of 4-ethynylbenzoic acid bridged in $\text{Cu}_4@\text{Cu}_3$ (B), coordination connection of outward extending carboxyl group with peripheral Cu (C), front (D) and side (E) views of dimer, and the total structure of $\text{Cu}_4@\text{Cu}_3$ (F)

Color code: Cu, green; P, violet and lilac; O, orange; C, light gray; H, light blue.

Cu—Cu in the Cu₃C₃ ring (3.81–3.83 Å) (Table S2 in the ESI), which indicates the electron-deficient nature of the three-center, two-electron Cu—C—Cu bonding. On the other hand, the copper atom in the Cu₃C₃ ring is relatively less electron-deficient due to its role in bridging the acetylene ligand in a μ_3 bridging manner and also engaging in side coordination with the acetylene group, which may contribute to Cu's *p* electron. The C—Cu₂—C bond angle is close to 102° (Table S3 in the ESI, Fig. 2A), with the carboxyl group extending outward, providing coordination conditions for the three Cu(I) in the outer coordination (Fig. 2C). It is noteworthy that one Cu of the three Cu (I) in the outer coordination is coordinated by CH₃O[−], rendering the cluster electrically neutral as a whole, in accordance with thermodynamic stability.

In addition, the compound exists as dimers, as shown in Fig. 2D. Two Cu₄@Cu₃ units are connected through weak interactions, such as C—H- π and hydrogen bonds between ligands, creating a molecular cage that looks like two tightly closed bowls (Fig. 2E). In this structure, the two Cu₄@Cu₃ units are arranged alternately and symmetrically, enhancing the overall stability of the cage (Fig. 2C). This arrangement not only maintains the integrity of the individual Cu₄@Cu₃ units but also promotes cooperation between them, resulting in a strong and functional molecular assembly.^[29,30]

3.2 UV-Vis Absorption and Steady-state Emission Spectroscopy

The solution-state photophysical properties of the staggered Cu₄@Cu₃ were recorded in MeOH (Fig. 3C). The Cu₄@Cu₃ absorbs UV light with wavelengths of around 300 nm, resulting in colorless solutions. It shows absorption maxima at around 345 nm.

We further detected the luminescent emission of Cu₄@Cu₃. Under the excitation of 396 nm light in the solid state, the emission spectrum of Cu₄@Cu₃ in Fig. 3A exhibited strong cyan emission centered at 484 nm. The quantum yield is 4.00%, and the emission lifetime at room temperature is 11.88 μ s (Fig. S4B in the ESI). In addition, Fig. 3B shows the excitation and emission spectra of

Cu₄@Cu₃ in the methanol solution. Under the excitation of 383 nm light, it exhibited red emission centered at 654 nm in the methanol solution. The quantum yield was measured to be 4.28% (Fig. S4A) in deaerated solution, and the emission lifetime was determined to be 6.68 μ s at room temperature. According to previous reports of similar core Cu₄ clusters,^[31] the phenomenon of dual emission in liquid and solid states is related to the rigid and relaxed states of these clusters. The high-energy (HE) bands should have the metal-perturbed intraligand (IL) [π - π^* (C $\equiv$ C—Ar)] character, while the low-energy (LE) band originated from ligand-to-metal charge transfer (LMCT) [π (C $\equiv$ C—Ar) $\rightarrow$ 4*s*/*p*(Cu)] and metal-centered (MC) [3*d* $\rightarrow$ 4*s*/*p*(Cu)] transitions.^[29] In addition, we also studied the variable temperature spectrum of the compound, and the solid-state emission spectra of the compound at 80–230 K are shown in Fig. 3D. Under the excitation of 396 nm light at 80 K, the high-energy spectrum band can be clearly observed. The emissions occur at 475 and 510 nm, with a vibrational frequency of 1453 cm^{−1}, which is typical of ν (C $\equiv$ C) stretches in the ground state.^[32] When the temperature ranges from 298 K to 80 K, the emission intensity gradually increases, and the lifetime also increases.

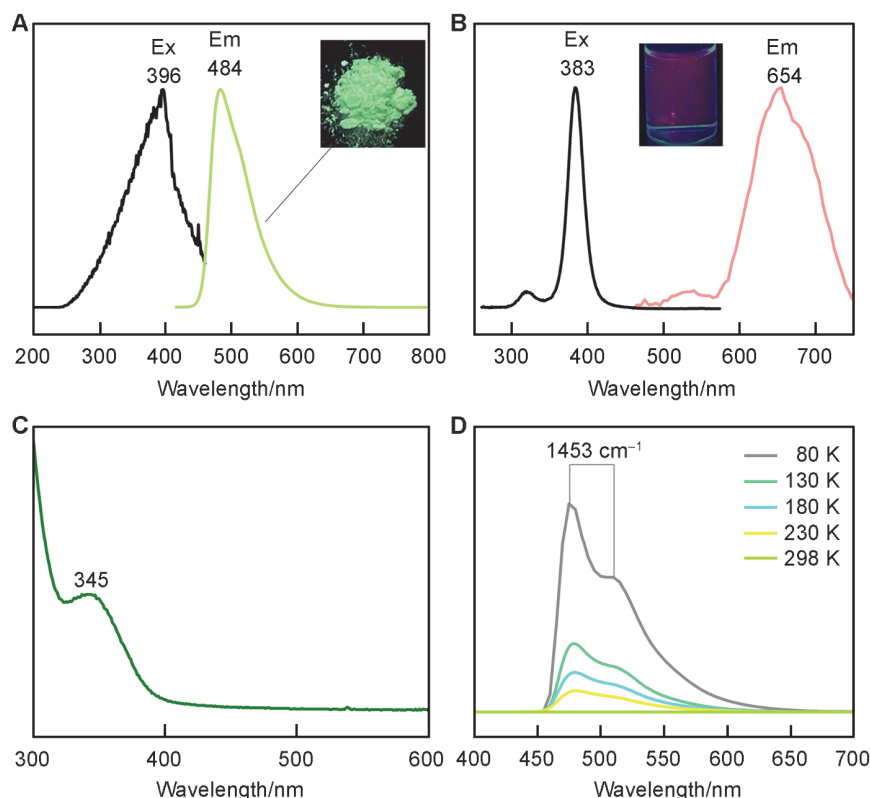


Fig. 3 Emission (Em) and excitation (Ex) spectra of Cu₄@Cu₃ in solid state at room temperature (A), Em and Ex spectra of Cu₄@Cu₃ dissolved in methanol solution at room temperature (*c*=8×10^{−4} mol/L) (B), UV-Vis spectra of crystals of Cu₄@Cu₃ dissolved in MeOH at room temperature (*c*=8×10^{−4} mol/L) (C), and variable temperature emission spectra in the solid state (D)

Inset in (A): the photographic image showing the emission color of Cu₄@Cu₃ in the solid state under 365 nm light; inset in (B): the photographic image showing the emission color of Cu₄@Cu₃ in methanol solution under 365 nm light.

Specifically, the lifetime is 71.32 μs at 180 K (Fig. S4C) and extends to 83.87 μs at 80 K (Fig. S4D). Additionally, the emission peak shows no significant red or blue shift, indicating a typical phosphorescent property.^[33]

3.3 AIE Phenomenon of $\text{Cu}_4\text{@Cu}_3$

The AIE properties of the cluster were evaluated by characterizing the luminescence properties of dilute solutions upon aggregation induced by the successive addition of H_2O , which acted as the poor solvent. Dissolve $\text{Cu}_4\text{@Cu}_3$ in methanol to obtain a completely dissolved substance. Different solutions with volume fractions of water (f_{water}) ranging from 0 to 80% were prepared while

maintaining a constant cluster concentration ($c=8\times 10^{-5}\text{ mol/L}$). Photographs of the solutions show increased emission intensity for higher water fractions (Fig. 4A) and this is a characteristic of the AIE property. When the f_{water} is less than 40%, the detected green light emission intensity hardly increases with the increasing of f_{water} . However, once the water content reaches 40%, strong green light emission will appear at 519 nm, while the red-light emission at 654 nm will almost disappear (Fig. 4B). This indicates the aggregation of the cluster monomer in the solution. The emission at 519 nm gradually increased, showing a progressive enhancement of the emission (Fig. 4C). The UV absorption results (Fig. 4D) show that in the water-dominated solution, the flat tail of the visible region can be clearly observed, confirming the formation of aggregates. Meanwhile, dynamic light scattering (DLS) measurement also shows that there are nanoaggregates with a size of about 103.7 nm in the solution with 90% f_{water} (Fig. 4E), while there are no aggregates in the methanol solution (Fig. S5 in the ESI).

3.4 X-Ray Scintillator

The radioluminescent (RL) properties of $\text{Cu}_4\text{@Cu}_3$ were investigated, as shown in Fig. 5B. $\text{Cu}_4\text{@Cu}_3$ in the solid state shows visible radioactive luminescence when exposed to an X-ray generator, akin to photoluminescence under ultraviolet excitation. The RL spectrum of the compound was recorded using a fluorescence spectrophotometer and an X-ray generator. Similar to the photoluminescence spectrum, the radioluminescence spectrum also exhibits a characteristic peak, and the peak of the compound occurs at 516 nm. In addition, the radioluminescence behavior of $\text{Cu}_4\text{@Cu}_3$ is linearly related to the X-ray dose rate. The luminous intensity of the compound shows a strong correlation with the X-ray intensity.

To comprehend the excited state characteristics of luminescent materials under high-energy X-ray

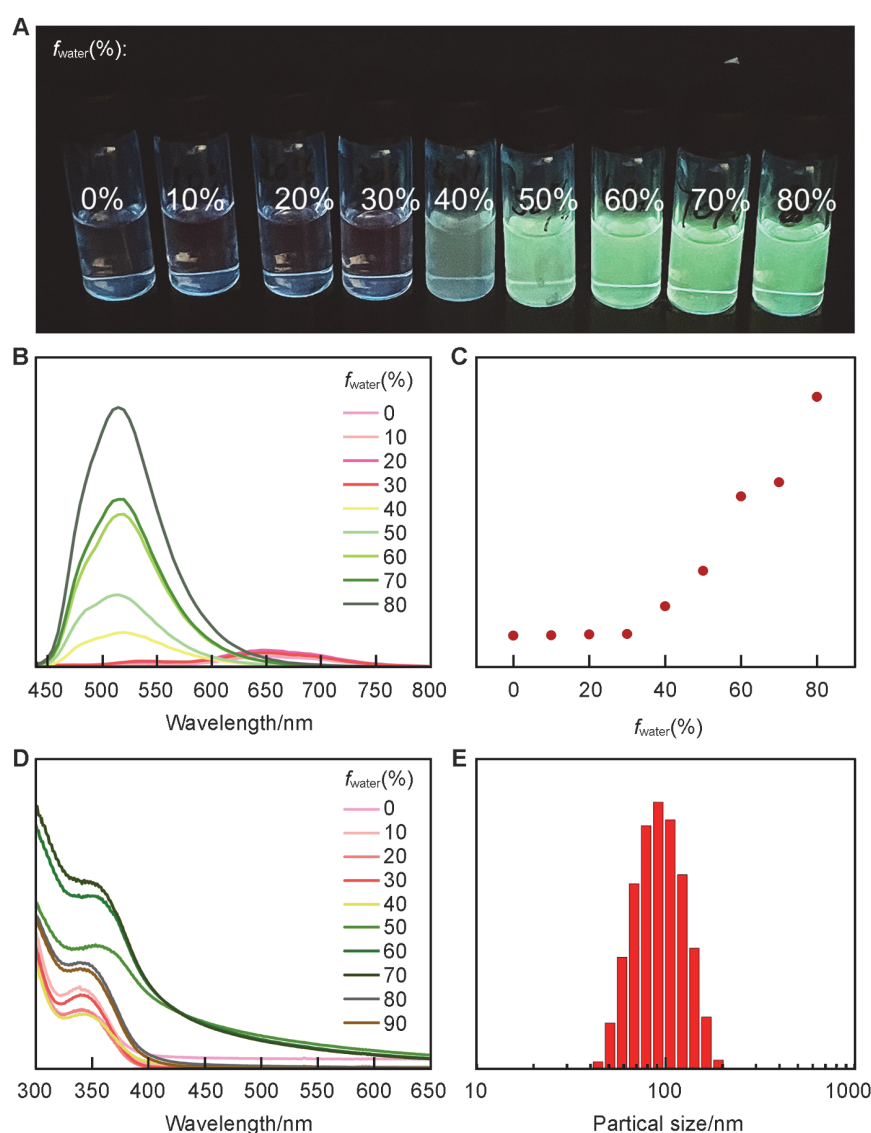


Fig.4 Photographs of increased emission intensity of solutions with higher water volume fractions (A), luminescence spectra of $\text{Cu}_4\text{@Cu}_3$ in $\text{H}_2\text{O}/\text{MeOH}$ mixtures with different f_{water} values (B), luminescence intensity of $\text{Cu}_4\text{@Cu}_3$ at 519 nm as a function of f_{water} (C), absorption spectra of $\text{Cu}_4\text{@Cu}_3$ in $\text{H}_2\text{O}/\text{MeOH}$ mixtures with different f_{water} values (D), and DLS results of $\text{Cu}_4\text{@Cu}_3$ in a 90% $\text{H}_2\text{O}/\text{MeOH}$ mixture (E)

Therefore, high radiation luminescence and high PL are typically observed.^[39]

4 Conclusions

In summary, we succeeded in obtaining and fully elucidating a novel luminescent nanocluster featuring a unique triangular pyramid with an open square structure, which exhibited photoluminescence dual emission in the visible region. The AIE phenomenon was observed in $\text{Cu}_4\text{@Cu}_3$, where the luminescence intensity in the aggregating state was higher than that in methanol solution. This discovery enriches the limited variety of atomically precise AIE clusters and offers the prospect of applications in multifunctional materials. The luminous intensity of $\text{Cu}_4\text{@Cu}_3$ has a strong correlation with X-ray intensity, making it a promising material for phosphorescent scintillators. These advancements could pave the way for developing functional materials using photoluminescent CuNCs.

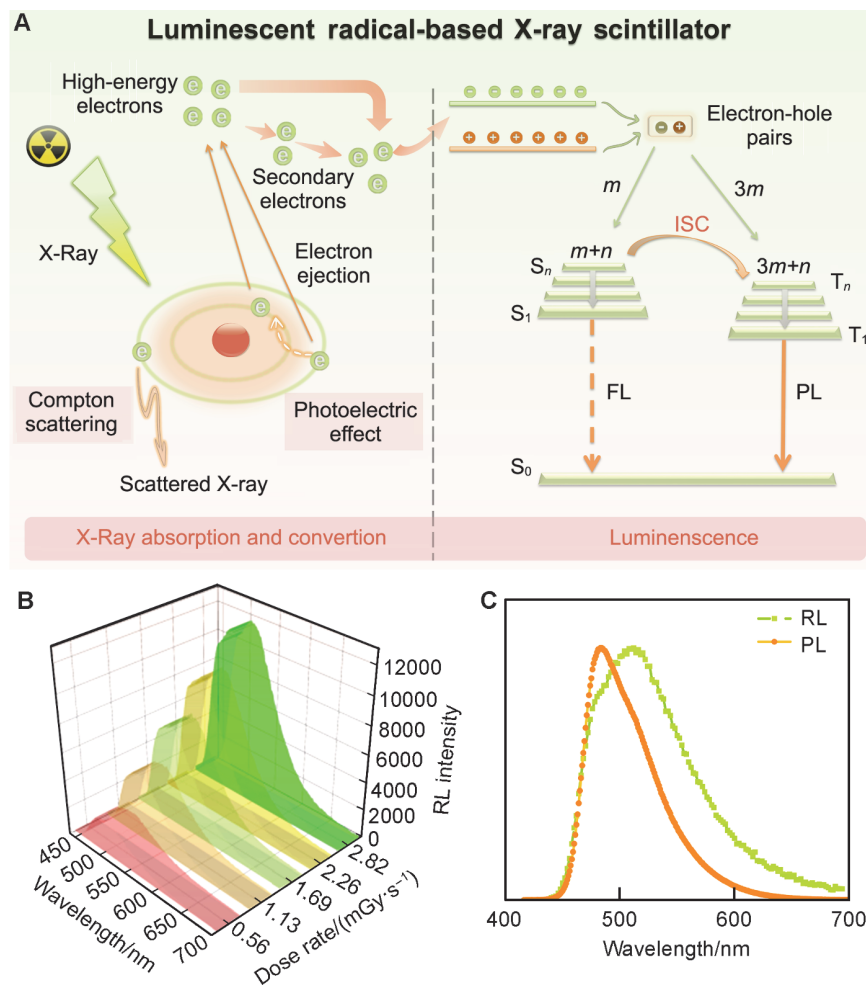


Fig. 5 Proposed RL mechanism (A), dosage-dependent radioluminescence spectra of $\text{Cu}_4\text{@Cu}_3$ (B), and comparison of PL and RL spectra of $\text{Cu}_4\text{@Cu}_3$ (C)

radiation and low-energy light excitation, we analyzed the PL and RL spectra of $\text{Cu}_4\text{@Cu}_3$ at 298 K (Fig. 5C). The spectra indicate that whether excited by ultraviolet or X-ray photons, the emission may come from the same excited state. Fig. 5A illustrates the luminescence mechanism of $\text{Cu}_4\text{@Cu}_3$ nanoclusters under X-ray irradiation. When the molecule is excited by X-rays, the nanoclusters initiate a scintillation process. During the absorption and conversion of X-rays, it primarily interacts with the heavy metal nuclei through the photoelectric effect and Compton scattering, resulting in the emission of high-energy electrons.^[34,35] Produced by electron-electron scattering and Auger processes, these hot electrons undergo rapid thermalization and are subsequently captured by organic ligands in the nanocluster scintillator. This interaction leads to the creation of hole-electron pairs and the subsequent cascade of secondary electrons.^[36] According to the law of spin conservation, the excitons produced by recombination are filled in triplet and singlet states in a ratio of 3:1.^[37,38] Finally, the radiation transition leads to singlet and triplet excitons producing fluorescence (FL) and phosphorescence (PL), respectively.

Electronic Supplementary Information

Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s40242-024-4137-y>.

Acknowledgements

This work was supported by the Natural Science Foundation of Hebei Province, China (No. B2023105031), the Natural Science Foundation of Beijing, China (No. 2232026), the High-level Overseas Youth Talents Program of China, and the Starting Grant from Beijing Institute of Technology, China.

We thank the staff of Beijing Zolix Instrument Co., Ltd. for their assistance with the X-ray scintillator experiments. The instrumental support from the Analysis and Testing Center of Beijing Institute of Technology, China is also highly appreciated.

Conflicts of Interest

The authors declare no conflicts of interest.

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